Inkjet Printing of Polymer Microspheres

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Abstract

Aqueous suspensions of colloidal polymer nanoparticles were deposited on glass substrates with different degrees of hydrophiliciy using a Dimatix DMP-2831 drop-on-demand (DoD) piezo-inkjet materials printer. The results are evaluated by optical means with respect to the final morphology governed by self-assembly processes.

1. Introduction and State-of-the-Art

Functional layers addressing more than only the human visual sense require both a microscopic texture and a defined nanoscopic structure at the same time. Photonic crystals made from colloidal materials can be seen as a layer with such an extended functionality as they affect the wave function of photons in a way similar to the way conventional semiconductors affect the wave function of electrons. Bragg diffraction in the bulk part of the crystalline layers gives rise to a directed and spectrally narrow photonic stop band in which the propagation of the photons is prohibited. Such functional layers are ascribed a key role in next-generation photon-based information technology [1] or recently an extension of this concept to acoustic phononic crystals [2]. For their manufacturing, bottom-up procedures based on self-assembly have been proven to be fast and facile methods to obtain a defined nanoscopic structure on a certain macroscopic area [3]. These methods comprise vertical deposition electrophoresis, gravity sedimentation, spin coating, fabrication in physical confinement cells, and others [4].

Beyond the named techniques, inkjet printing has certain properties to make it an attractive production technique. Provided the colloidal raw material can be rendered an ink suitable for liquid deposition, it is – at least in the ideal case – deposited only at loci on the substrates where it is absolutely necessary. Such a direct-write approach is charming especially when (i) the run lengths of an application are small or even (ii) a personalization of manufactured items is required, and/or (iii) simply the materials to be deposited are very expensive. For inkjet-printed colloidal materials, the self-assembly is governed by the evaporation of droplets on their way towards and of the sessile drops on pre-treated substrate.

Nontheless, the number of attempts that elucidate the role of additive liquid-based manufacturing techniques that exploit both, the liability of appropriate photonic building blocks to self-assembly and the technical advantages of inkjet printing, are comprehensible. The state of the art is determined in substance by Park and Moon [5-8]. Park and Moon did initial studies on the formation of colloidal crystal structures using silica [5; 8] and polymer [6; 7] colloidal suspensions. In their studies, variable parameters are the particle diameter, solids content, and ink composition. Substrates are (oxidized) silicon, in part covered with a hydrophobic molecular layer. Photonic functionality and quality of the printed single drops were characterized using microreflectance spectroscopy. Inter alia it has been shown, that the structural and photonic quality shifts as a function of the particle size [6] and ink composition [8]. Consecutively, Perelaer et al. reported on inkjet printing of suspensions containing silica microspheres with emphasis on the particular contact-line behaviour [9]. Besides inkjet printing, microspotting has gained a current attraction [10; 11].

In this paper we report on inkjet printing of monodisperse polystyrene microsphere particles suspended in an aqueous environment at two different solids contents on glass substrates of different surface energy at variable drop spaces with a Dimatix DMP-2831 drop-on-demand (DoD) piezo-inkjet materials printer. The aim of this contribution was the fabrication of single-drop crystals consisting of ordered multilayers.

2. Experimental

Colloidal inks were used containing highly monodisperse polystyrene microsphere particles suspended in an aqueous environment. The suspensions were obtained from Duke Scientific {Palo Alto, CA, USA 0.1 % solids content, (300±5) nm particle diameter, (57.3±0.9) mN/m surface tension} and BS-Partikel GmbH {Wiesbaden, Germany, 2.0 % solids content, particle diameter (305±8) nm, (46.8±0.8) mN/m surface tension}. The surface tension of the inks was determined by an OCA20 (dataphysics, Filderstadt, Germany) contact-angle measurement system (Table 1).

Coverslip glasses were used as substrates. All substrates were cleaned in ethanol and then rinsed with deionized water and dried under a flow of air before the chemical or physical treatment. The contact angles on all surfaces were measured with pure water droplets (using also dataphysics OCA20, sessile-drop modus). The following surface modifications were applied: (i) no further treatment ("untreated"), (ii) surfactant treatment, (iii) corona treatment, (iv) hexamethyldisilazane (HMDS) treatment, (v) octadecyltrichlorosilane (OTS) treatment. The surfactant treatment, HMDS treatment and OTS treatment were done in a chemical bath according to known methods. Corona treatment was performed using a high voltage discharge (2.3 kV).

Table 1: Contact angle on the different surface modifications

contact angle with pure water				
corona treated	surfactant treated	untreated	HMDS treated	OTS treated
< 10°	< 10°	67,7° ± 2,7°	78,7° ± 1,5°	100° ± 5°

From the contact angle results in Table 1 it is shown that HMDS and OTS treatments decrease the surface energy, whereas surfactant and corona treatment increase the surface energy.

The colloidal inks containing monodisperse polystyrene microspheres were printed by using a Dimatix DMP-2831 laboratory drop-on-demand (DoD) piezo-inkjet materials printer (Fujifilm Dimatix Inc., Santa Clara, USA). The system setup consisted of a piezoelectric DoD inkjet nozzle with a 21.5 µm orifice and a nominal drop volume of 10 pl. The clear distance between the nozzle and the substrate surface was maintained at 1 mm during printing. All samples were printed at ambient conditions {(22.3±2) °C and (25.0±4) % relative humidity}. The DMP has a build-in stroboscopic drop watcher to allow for a determination and optimization of the droplet formation. A ball-shaped regular droplet ejection was achieved at a voltage of (18±2) V, 3 kHz frequency and a pulse width of (11.5±0.5) µs.

The inks were printed on the differently treated glass slides. The test pattern consisted of single droplets with varying dot-to-dot spaces. The droplets morphology was investigated with optical microscopy, confocal laser-scanning microscopy (both Zeiss LSM 510), and scanning electron microscopy (SEM, Hitachi TM-1000).

3. Results and Discussion

Figure 1 shows an overview of typical printing results for each treatment and solids content; Table 2 represents some parameters of the printed single droplets. For the droplets on corona treated, surfactant treated, untreated and HMDS treated substrates certainly a higher concentration of the particles is recognizable by the outer zone in all structures. This appearance represents the in inkjet technology often investigated coffee ring effect. It occurs in particular increasingly at the surfactant and the corona-treated substrates. In these two cases, the center of the single droplet structures is almost particle-free.

In the SEM results, the single droplets with 2% solids content on OTS do not have any remarkable or increased edge structure compared to the other substrates. The center of the deposited drop is filled with particle uniformly. Here it results in a very homogeneous layer with some dot and line defects. It becomes clear that, on the OTS substrates in comparison with the remaining treatment methods other self-assembly mechanisms are important. Table 2 presents the parameters of the printed single droplets derived from the optical measurements.

Regarding the reproducibility of the deposited droplets, a printed line consisting of 20 sequentially printed droplets was optically investigated. The excentricity of each droplet was determined by an approximation with a superseding circle at maximum overlap and measuring the droplet diameter via four fixed diameters. Figure 2 shows the results of the measurement, with the standard devation for each droplet indicated. It turns out, that the drop-to-drop variation in diameter is of the order of 0.5 µm (amounting thus 5 % of the total diameter). The typical excentricity is in the range of 0.2 µm.

4. Summary and Outlook

The results of the characteristics of the single droplets observed as a function of the surface energy of the substrates are summarized in Table 3. It turns out that a high substrate surface energy (as it is the case for corona and surfactant treated substrates) causes a high drop diameter due to the higher spreading of the suspensions in comparison with substrates of low surface energy. The surface energy affects also the circularity of the structure. In particular, for HMDS and OTS treated substrates, almost ideal circle formation (see also Figures 1 and 2) could be found. Correspondingly, the coffee-ring effect is observed at low substrate surface energies at small contact angles, whereas angles above 90° necessitate a behavior counteracting the coffee ring effect.

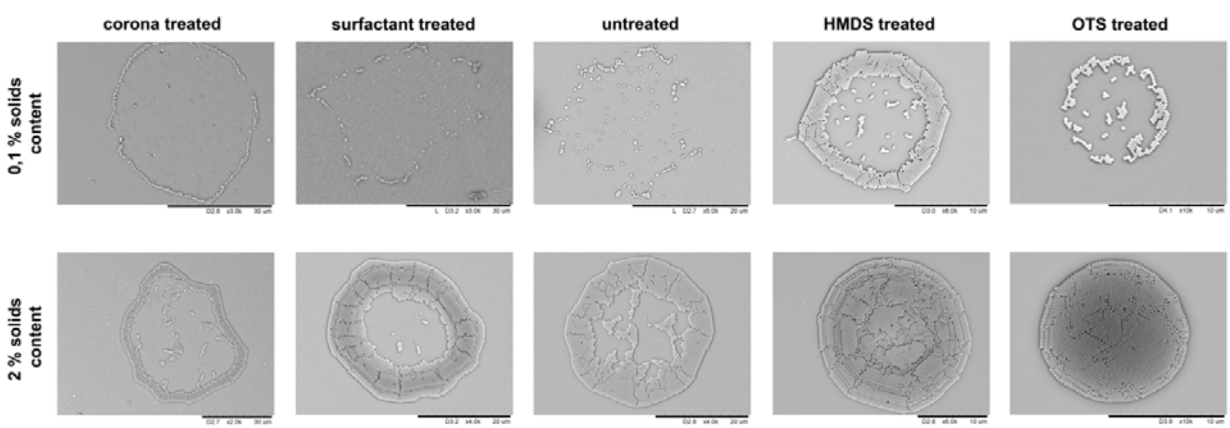

***Figure 1:** Comparison of the single droplet morphology with variation of substrate treatment and solids content*

Table 2: Parameters of the single droplets (using scanning electron microscopy pictures; numbers of layers determined by count)

	corona treated		surfactant treated		untreated		HMDS tretated		OTS treated	
solids content	0.1 %	2 %	0.1 %	2 %	0.1 %	2 %	0.1 %	2 %	0.1 %	2 %
diameter [µm]	50	52	41	33	22	32	16	24	9	12
layers	1	1	1	2-3	1	1-4	1	2-3	1	2-3

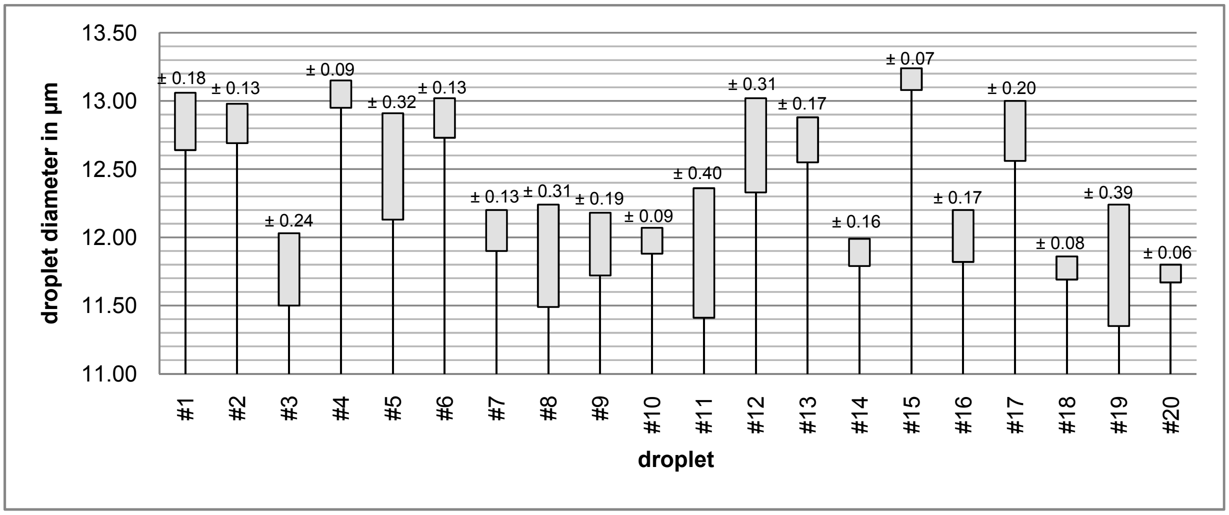

Figure 2: *Droplet diameter (position of bars) and excentricity (height of bars) exemplified for 20 drops printed sequentially in a line on an OTS-treated glass substrate at 2% solids content*

Table 3: Results of the single droplet structures in dependence of the substrate surface energy ("-" sign: small/little/low; "+" sign: high/much/strong)

substrate surface energy	diameter	circularity	coffee-ring effect appropriate behavior	particle layers	particle-filling of the structure
high	+	-	+	-	-
low	-	+	-	+	+

The area coverage of the drops is strongly dependent on the treatment of the substrates. If the suspension spreads more strongly (as for corona and surfactant treated substrates), a smaller contact angle restricts the multilayer-formation and the large circumference prohibits full area coverage. A contrary development is to be noted at substrates with higher contact angles where the contact line recedes during the evaporation process. Regarding a full area-coverage and multilayer formation, deposition of 2% solids contend suspensions on OTS-treated substrates gave the best results. Furthermore, a variation of the particular ink composition as well as clear distances are to be performed in order to adapt the self-assembly properties of rather all participating materials (building blocks, substrates, surfactants, and diluent) governing the relevant structure-property relationships. In future it is still necessary to proof the photonic functionality [12] of the printed layers and to identify possible applications [13].

5. References

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